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What does Electrode Particle Size have to do with High Power Lithium-Ion Batteries?

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High power Li-ion batteries presently enjoying a healthy market in power tools are expected to play prominent roles in the next generation hybrid and plug-in-hybrid electric vehicles (HEV and PHEV), as well as military and aerospace applications including the Joint Strike Fighter aircrafts and Directed Energy Weapons. Consequently, knowledge of the fundamental principles governing the design and fabrication of high power Li-ion batteries is important for developing batteries with optimum power to energy ratios for these applications. Lithium-ion batteries for HEV are expected to experience charge and discharge at the 20-30C rates whereas those for PHEV, because of their larger energy content, would be charged and discharged at the 3-5C rates.

The power (P) of a battery is given by Power (P) = V.I, where V is the load voltage and I is the current drawn from the battery. Since V = I.R from Ohm's law, $P = V^2 / R$. It is clear that the key to design a high power battery is to maximize its voltage, V, and minimize its internal resistance, R.

The load Voltage, V, is the difference between the open circuit voltage E and the voltage drop (ΔE) due to all the polarization losses in the cell including voltage drop due to electrolyte and separator resistances, anode and cathode resistances including their contact resistances, the resistances of the passivation films (solid electrolyte interphases, SEI) on the cathode and anode, charge transfer (activation) over-potential of the anode and cathode, and, finally, voltage losses arising from Li^+ concentration polarization in the electrolyte.

For pulse power applications involving one to seconds or shorter pulses, the main contributors to the voltage loss in the cell are the Ohmic resistances of the electrolyte, separator, electrodes and current collector contacts.

For continuous high power discharge and charge, Li ion concentration polarization in the electrolyte present in the separator and the porous electrode, and Li ion diffusion rates in the electrode materials also become important. The Li ion diffusion coefficient, D_{solid} , determines the minimum particle size of the electrode materials required for their full utilization at the highest rates of charge and discharge. $D_{solid} = l^2/t$ where l is the radius of an electrode particle and t is the time required for the Li ion to fully diffuse into it. When $D_{solid} = 10^{-9}$ - 10^{-10} cm^2/sec (as in layered electrode materials such as $LiCoO_2$, $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ and graphite), the average particles have to be in the 1-5 micron range or less in order to achieve full utilization in 60 sec. On the other hand if $D_{solid} = 10^{-13}$ to 10^{-14} cm^2/sec as in $Li_4Ti_5O_{12}$ and $LiFePO_4$, the particles have to be on the order of ~ 15-120 nm to realize full capacity in 60 sec. The electrode material particle size required is chosen for the highest continuous power draw from the battery

It is clear that the need for nano or micron size particles depend on the Li ion diffusion coefficients in the solid electrode particles and the desired discharge power of the battery. Indeed, commercial high power Li-ion batteries based on nano-size $LiFePO_4$ positive electrodes characterized by low D_{solid} are built in combination with micron size graphite negative electrodes in which D_{solid} is usually a factor of four to five higher. Similarly, high power Li-on batteries utilizing nano-size $Li_4Ti_5O_{12}$ negative electrodes having very low D_{solid} (~ 10^{-14} cm^2/sec) are built with micron size layered metal oxide positive electrode materials such as $LiCoO_2$ and $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$, which exhibit high D_{solid}. The Ragone plots in Figure 1 compare the power to energy profiles of the aforementioned $LiFePO_4$ cell with those of the graphite/$LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ and graphite/LiMn2O4 cells in which both negative and positive electrodes are made up of micron size particles. All cells show very similar power capability.

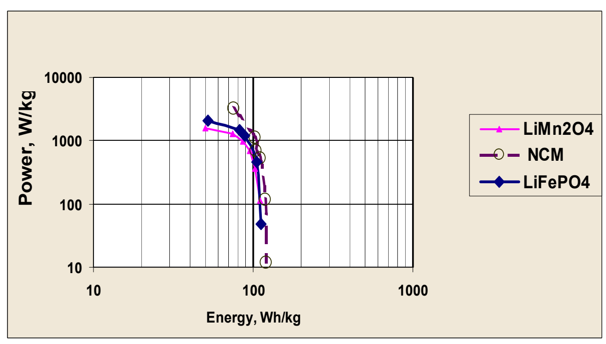

Figure 1: *Ragone plots for a 3 Ah graphite/ $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ cell and commercial 26650cells with $LiFePO_4$ and $LiMn_2O_4$ cathodes. The $LiFePO_4$ cell utilizes nano size positive electrode and micron size negative electrode materials. The positive and negative electrodes in the $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ and $LiMn_2O_4$ cells are composed of micron size particles.*

The discharge rate capability desired for Li-ion batteries for HEV and HEV can be achieved with micron or nano size electrode materials depending on the Li ion diffusion coefficients of the solid electrode materials chosen. Once the appropriate electrode materials are chosen, the properties of the electrolyte, separator and current collectors are optimized to achieve the desired power to energy profiles from the battery. A difficult issue with HEV and PHEV Li-ion batteries is to achieve the same high charge rate as the discharge, particularly at low temperatures. The rate-limiting electrode for charge in a lithium ion battery is the graphite negative electrode. Optimization of the composition of the electrolyte and the properties of the SEI layer on the negative electrode could overcome charge rate limitations.

Reference

K.M. Abraham et al, J. Electrochem. Soc. 145, 482 (1998)